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Absolute Configuration of (*S*)-(+)-[(Benzyl-oxymethyl)(*tert*-butyl)methylsilyl] Methyl Ketone

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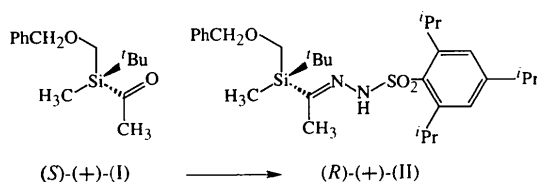
(Received 20 September 1995; accepted 16 October 1995)

Abstract

The absolute configuration of the title compound was confirmed by an X-ray crystal structure analysis of (*R*)-(+)-[(benzyloxymethyl)(*tert*-butyl)methylsilyl] methyl ketone 2,4,6-trisopropylphenylsulfonylhydrazone, $C_{30}H_{48}N_2O_3SSi$, reported herein. The asymmetric unit of the hydrazone contains two molecules which are linked by intermolecular hydrogen bonds.

Comment

We have recently demonstrated that chiral acylsilanes of type (I) can be efficiently used as starting materials for the stereoselective preparation of α -hydroxysilanes (Bienz & Chapeaurouge, 1991; Chapeaurouge & Bienz, 1993). The latter compounds can be transformed into silicon-free secondary alcohols (Bienz *et al.*, 1995) or they can be used as starting materials for other stereospecific transformations (Enev, Stojanova & Bienz, 1995).



Optically active (*S*)-(+)-[(benzyloxymethyl)(*tert*-butyl)methylsilyl] methyl ketone, (*S*)-(+)-(I), and its optical antipode are accessible by a route involving a bioreduction step (Bienz *et al.*, 1995). The absolute configuration at the chiral silicon centre in each of these compounds was determined by a combination of the empirical Mosher method and Nuclear Overhauser Effect (NOE) experiments. However, the NOE effects upon which the assignments are based are rather weak. Therefore, in order to secure unambiguously the absolute configuration of (*S*)-(+)-(I), the X-ray structure of its hydrazone derivative, (*R*)-(+)-(II), was determined.

The asymmetric unit of (II) contains two molecules, A and B, of the same enantiomorph. Views of molecules A and B, showing the atomic numbering and the correct absolute configuration, are given in Fig. 1. The absolute configuration was determined by refinement of the structure and the absolute-structure parameter (Flack, 1983), as described in the *Experimental*. Both

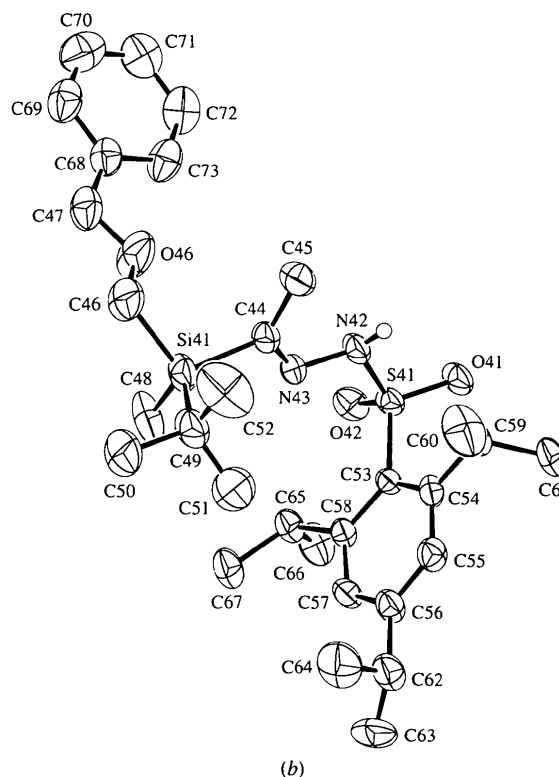
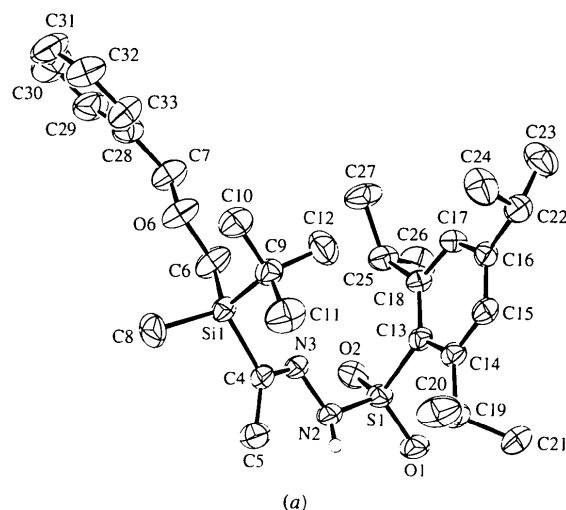


Fig. 1. Views of (a) molecule A and (b) molecule B showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Most of the H atoms have been omitted for clarity.

molecules have similar bond lengths and angles. Except for atoms O6, C7, C10, C11, C12 and C28–C33, the non-H atoms in molecule *A* are related by a pseudo-centre of inversion to the corresponding atoms in molecule *B*, but additional crystallographic symmetry is not present.

The symmetry-independent molecules are linked into dimeric units by intermolecular hydrogen bonds (Table 2). The N–H groups of molecules *A* and *B* act as donors, with one of the sulfonyl O atoms from molecules *B* and *A*, respectively, acting as the acceptors.

Experimental

A solution of 56 mg (0.21 mmol) of (*S*)-(+)-**I** (Bienz *et al.*, 1995) and 66 mg (0.22 mmol) of 2,4,6-triisopropylphenyl-sulfonylhydrazine in 5 ml of dry acetonitrile was stirred at 296 K under nitrogen for 3 h. The solvent was evaporated and the residue chromatographed (SiO₂, hexane/ethyl acetate 25:1) to give 102 mg (0.18 mmol, 88%) of crystalline (*R*)-(+)-**II**, which was recrystallized from 2-propanol (m.p. 364–367 K); [α]_D²³ +20° (tetrahydrofuran, *c* 1.0). ¹H NMR (CDCl₃, 300 MHz): δ (p.p.m.) 7.37–7.21 (*m*, 5H, 5 \times aromatic CH), 7.13 (*s*, 2H, 2 \times aromatic CH), 4.38 (*s*, 2H, PhCH₂O), 4.18 (*h*, *J* = 6.8 Hz, 2H, 2 \times CH), 3.27 (*s*, 2H, SiCH₂O), 2.80 (*h*, *J* = 6.7 Hz, 1H, CH), 1.79 (*s*, 3H, CH₃), 1.25–1.22 (*m*, 18H, 6 \times CH₃), 0.69 [*s*, 9H, C(CH₃)₃], 0.05 (*s*, 3H, SiCH₃); ¹³C NMR [CDCl₃, 50.4 MHz, multiplicities from 'distortionless enhancement by polarization transfer' experiments, atom numbering as in Fig. 1(*a*)]: δ (p.p.m.) 160.8 (*s*, C4), 153.2 (*s*, C13), 150.9 (*s*, 2C, C14 and C18), 138.6 (*s*, C16), 131.1 (*s*, C18), 128.2 (*d*, 2C, C29 and C33), 127.4 (*d*, 2C, C30 and C32), 127.3 (*d*, C31), 123.5 (*d*, 2C, C15 and C17), 77.1 (*t*, C7), 59.9 (*t*, C6), 34.2 (*d*, C22), 29.7 (*d*, 2C, C19 and C25), 26.5 (*q*, 4C, C20, C21, C26 and C27), 24.7 (*q*, 3C, C10, C11 and C12), 23.6 (*q*, 2C, C23 and C24), 17.0 (*s*, C9), 19.3 (*q*, C5), –9.5 (*q*, C8); CI–MS (NH₃): *m/z* 545 [*M* + 1]⁺. Crystals suitable for the X-ray analysis were obtained by recrystallization from hexane with 5% methanol.

Crystal data

C₃₀H₄₈N₂O₃SSi

M_r = 544.87

Triclinic

*P*1

a = 10.890 (1) Å

b = 17.714 (3) Å

c = 8.940 (1) Å

α = 97.24 (1)°

β = 105.824 (8)°

γ = 93.82 (1)°

V = 1636.8 (4) Å³

Z = 2

D_x = 1.106 Mg m^{–3}

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 18–20°

μ = 0.165 mm^{–1}

T = 243 (1) K

Prism

0.38 \times 0.35 \times 0.35 mm

Colourless

Data collection

Rigaku AFC-5R diffractometer

*R*_{int} = 0.1165

θ_{\max} = 27.5°

$\omega/2\theta$ scans

Absorption correction:

none

13 818 measured reflections

13 158 independent reflections

9678 observed reflections
[*F*² > 2σ(*F*²)]

h = –11 → 14

k = –22 → 22

l = –11 → 11

3 standard reflections
monitored every 150
reflections

intensity decay:
insignificant

Refinement

Refinement on *F*²

R(*F*) = 0.0501

wR(*F*²) = 0.1446

S = 1.012

13 157 reflections

698 parameters

w = 1/[σ²(*F*_o²) + (0.0712*P*)²
+ 0.2780*P*]

where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} = 0.30

Δρ_{max} = 0.23 e Å^{–3}
Δρ_{min} = –0.32 e Å^{–3}

Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Absolute configuration:
Flack (1983) parameter
= –0.02 (7)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Si1	0.45900 (7)	0.94550 (5)	1.26160 (9)	0.0449 (2)
Si1	0.90769 (9)	0.84619 (6)	1.36163 (12)	0.0479 (2)
O1	0.3988 (2)	1.00939 (15)	1.3153 (3)	0.0582 (7)
O2	0.4267 (3)	0.9215 (2)	1.0974 (3)	0.0563 (7)
O6	0.8970 (3)	0.72453 (15)	1.1429 (3)	0.0684 (7)
N2	0.6132 (3)	0.9744 (2)	1.3247 (4)	0.0482 (7)
N3	0.6922 (3)	0.9159 (2)	1.3106 (4)	0.0459 (7)
C4	0.8129 (4)	0.9311 (2)	1.3789 (4)	0.0486 (9)
C5	0.8744 (4)	1.0088 (2)	1.4695 (6)	0.0684 (12)
C6	0.8247 (5)	0.7865 (3)	1.1677 (5)	0.0719 (12)
C7	0.8444 (4)	0.6754 (2)	1.0007 (4)	0.0695 (11)
C8	1.0756 (4)	0.8804 (3)	1.3664 (7)	0.0821 (14)
C9	0.9102 (4)	0.7921 (2)	1.5320 (5)	0.0550 (9)
C10	1.0011 (4)	0.7293 (3)	1.5349 (5)	0.0726 (12)
C11	0.9571 (6)	0.8469 (3)	1.6871 (5)	0.093 (2)
C12	0.7744 (5)	0.7544 (3)	1.5142 (7)	0.0859 (15)
C13	0.4350 (3)	0.8666 (2)	1.3638 (4)	0.0395 (7)
C14	0.4525 (3)	0.8828 (2)	1.5278 (4)	0.0447 (8)
C15	0.4324 (4)	0.8222 (2)	1.6057 (4)	0.0484 (9)
C16	0.3959 (4)	0.7476 (2)	1.5298 (4)	0.0437 (8)
C17	0.3805 (4)	0.7342 (2)	1.3710 (4)	0.0460 (8)
C18	0.4010 (3)	0.7912 (2)	1.2827 (4)	0.0414 (8)
C19	0.4982 (4)	0.9617 (2)	1.6313 (5)	0.0566 (10)
C20	0.6186 (5)	0.9577 (3)	1.7623 (7)	0.097 (2)
C21	0.3910 (5)	0.9886 (3)	1.7010 (6)	0.0730 (13)
C22	0.3852 (4)	0.6829 (2)	1.6248 (5)	0.0569 (10)
C23	0.2886 (5)	0.6152 (3)	1.5385 (6)	0.0847 (15)
C24	0.5154 (5)	0.6570 (3)	1.6878 (7)	0.088 (2)
C25	0.3841 (4)	0.7650 (2)	1.1077 (4)	0.0546 (10)
C26	0.2446 (5)	0.7694 (3)	1.0134 (5)	0.0730 (12)
C27	0.4248 (6)	0.6846 (3)	1.0759 (5)	0.0796 (15)
C28	0.9371 (4)	0.6192 (2)	0.9765 (4)	0.0599 (10)
C29	0.9390 (6)	0.5915 (3)	0.8258 (5)	0.0789 (14)
C30	1.0253 (8)	0.5405 (4)	0.8024 (7)	0.113 (2)
C31	1.1092 (6)	0.5177 (3)	0.9269 (8)	0.103 (2)
C32	1.1078 (6)	0.5443 (3)	1.0754 (7)	0.092 (2)
C33	1.0227 (5)	0.5944 (3)	1.1006 (5)	0.0739 (12)
S41	0.60242 (7)	0.19011 (5)	0.58597 (9)	0.0464 (2)
Si41	0.16258 (11)	0.28851 (7)	0.53322 (15)	0.0656 (3)
O41	0.6629 (2)	0.12783 (15)	0.5256 (3)	0.0594 (7)
O42	0.6408 (3)	0.2129 (2)	0.7527 (3)	0.0609 (7)
O46	0.0545 (3)	0.1987 (2)	0.6862 (5)	0.1082 (12)
N42	0.4492 (3)	0.1596 (2)	0.5278 (4)	0.0524 (8)
N43	0.3721 (3)	0.2176 (2)	0.5518 (4)	0.0507 (8)

C44	0.2508 (4)	0.2038 (2)	0.4912 (5)	0.0522 (9)
C45	0.1861 (4)	0.1291 (3)	0.3945 (7)	0.0764 (14)
C46	0.0127 (5)	0.2502 (3)	0.5772 (7)	0.0891 (15)
C47	-0.0263 (4)	0.1819 (3)	0.7739 (6)	0.0792 (12)
C48	0.2637 (6)	0.3511 (4)	0.7144 (7)	0.106 (2)
C49	0.1279 (5)	0.3406 (3)	0.3616 (6)	0.0802 (14)
C50	0.0448 (7)	0.4064 (4)	0.3875 (9)	0.119 (2)
C51	0.2526 (6)	0.3757 (4)	0.3392 (9)	0.120 (2)
C52	0.0511 (8)	0.2856 (4)	0.2100 (7)	0.139 (3)
C53	0.6208 (3)	0.2716 (2)	0.4889 (4)	0.0406 (7)
C54	0.6045 (3)	0.2582 (2)	0.3260 (4)	0.0468 (9)
C55	0.6243 (4)	0.3212 (2)	0.2527 (4)	0.0561 (10)
C56	0.6524 (4)	0.3957 (2)	0.3320 (5)	0.0568 (10)
C57	0.6639 (4)	0.4064 (2)	0.4910 (4)	0.0535 (9)
C58	0.6469 (4)	0.3478 (2)	0.5738 (4)	0.0434 (8)
C59	0.5666 (4)	0.1810 (2)	0.2200 (5)	0.0566 (10)
C60	0.4448 (5)	0.1835 (4)	0.0836 (7)	0.110 (2)
C61	0.6751 (5)	0.1551 (3)	0.1547 (6)	0.0782 (14)
C62	0.6613 (6)	0.4627 (3)	0.2432 (5)	0.0759 (14)
C63	0.7582 (7)	0.5299 (3)	0.3373 (8)	0.102 (2)
C64	0.5255 (7)	0.4864 (4)	0.1821 (8)	0.108 (2)
C65	0.6541 (4)	0.3704 (2)	0.7483 (4)	0.0523 (9)
C66	0.7884 (5)	0.3706 (3)	0.8531 (5)	0.0750 (13)
C67	0.6057 (5)	0.4489 (3)	0.7781 (5)	0.0683 (12)
C68	0.0125 (4)	0.1176 (3)	0.8614 (5)	0.0642 (10)
C69	-0.0695 (5)	0.0862 (3)	0.9392 (6)	0.0807 (14)
C70	-0.0387 (6)	0.0266 (4)	1.0169 (6)	0.096 (2)
C71	0.0747 (6)	-0.0054 (4)	1.0201 (6)	0.091 (2)
C72	0.1557 (5)	0.0246 (3)	0.9464 (5)	0.0831 (14)
C73	0.1260 (4)	0.0855 (3)	0.8670 (5)	0.0764 (13)

Table 2. *Selected geometric parameters (\AA , $^\circ$)*

Si1—O1	1.440 (3)	S41—O41	1.444 (3)	
Si1—O2	1.414 (3)	S41—O42	1.430 (3)	
Si1—N2	1.642 (3)	S41—N42	1.638 (3)	
Si1—C13	1.806 (3)	S41—C53	1.802 (3)	
Si1—C4	1.895 (4)	Si41—C44	1.888 (4)	
Si1—C6	1.870 (5)	Si41—C46	1.884 (5)	
Si1—C8	1.874 (4)	Si41—C48	1.865 (6)	
Si1—C9	1.895 (4)	Si41—C49	1.853 (5)	
O6—C6	1.422 (5)	O46—C46	1.422 (6)	
O6—C7	1.399 (4)	O46—C47	1.370 (5)	
N2—N3	1.406 (4)	N42—N43	1.401 (4)	
N3—C4	1.283 (5)	N43—C44	1.277 (5)	
C4—C5	1.516 (6)	C44—C45	1.501 (6)	
C7—C28	1.503 (5)	C47—C68	1.482 (6)	
O1—Si1—O2	117.1 (2)	O41—S41—O42	116.9 (2)	
N2—Si1—C13	105.9 (2)	N42—S41—C53	106.2 (2)	
C4—Si1—C6	106.6 (2)	C44—Si41—C46	107.1 (2)	
C4—Si1—C8	109.7 (2)	C44—Si41—C48	108.7 (2)	
C4—Si1—C9	108.6 (2)	C44—Si41—C49	109.2 (2)	
C6—Si1—C8	109.8 (3)	C46—Si41—C48	107.5 (3)	
C6—Si1—C9	112.0 (2)	C46—Si41—C49	112.8 (2)	
C8—Si1—C9	110.1 (2)	C48—Si41—C49	111.5 (3)	
C6—O6—C7	114.6 (3)	C46—O46—C47	116.0 (3)	
Si1—N2—N3	113.9 (2)	S41—N42—N43	112.5 (3)	
N2—N3—C4	117.6 (3)	N42—N43—C44	118.3 (3)	
Si1—C4—N3	113.6 (3)	Si41—C44—N43	112.5 (3)	
Si1—C4—C5	122.7 (3)	Si41—C44—C45	123.8 (3)	
N3—C4—C5	123.7 (3)	N43—C44—C45	123.7 (4)	
Si1—C6—O6	109.1 (3)	Si41—C46—O46	105.1 (3)	
O6—C7—C28	109.9 (3)	O46—C47—C68	112.0 (4)	
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O41 ⁱ	0.88 (3)	2.14 (3)	2.991 (4)	162 (2)
N42—H42...O1 ⁱⁱ	0.89 (2)	2.20 (3)	2.993 (4)	148 (2)

Symmetry codes: (i) $x, 1+y, 1+z$; (ii) $x, y-1, z-1$.

The data collection was extended to include the measurement of the intensities of the Friedel opposites of those reflections in the unique hemisphere for which $\theta < 25^\circ$. The amine H atoms were located in a difference electron density map and refined isotropically with bond-length restraints of 0.90 (1) \AA . All other H atoms were placed in geometrically calculated

positions and allowed to ride on their respective parent C atom, with fixed isotropic displacement parameters equal to $1.2U_{\text{eq}}$ of the parent C atom ($1.5U_{\text{eq}}$ for methyl groups). The origin was fixed by using the least-squares-restraints method of Flack & Schwarzenbach (1988). For the determination of the absolute configuration, the *TWIN* and *BASF* options of *SHELXL93* (Sheldrick, 1993) were used in the final refinement to refine the absolute-structure parameter (Flack, 1983). The refined value confidently confirms that the atomic coordinates represent the correct enantiomorph. A refinement of the structure using the centrosymmetric space group $P\bar{1}$ showed that many of the non-H atoms of molecule *A* are almost perfectly related by a centre of inversion to the corresponding atoms in molecule *B*. However, atoms O6, C7, C10, C11, C12 and C28–C33 can only be refined in $P\bar{1}$ if they are included as disordered atoms, whereas the structure could be refined without disorder in the non-centrosymmetric space group *P1*. The presence of a racemic crystal and additional crystallographic symmetry can therefore be discounted.

MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* (Molecular Structure Corporation, 1989) was used for data reduction. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined with *SHELXL93*. The molecular graphics were produced using *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1320). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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